REACTIONS OF PERHALOCARBONS. PART IX.
CONVERSION OF PER(POLY)FLUOROALKYL HALIDES INTO THE CORRESPONDING CARBOXYLIC ACIDS WITH A REDOX SYSTEM

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SUMMARY

The conversion of per(poly)fluoroalkyl halides into the corresponding carboxylic acids with a redox system-$(NH_4)_2S_2O_8/HCO_2Na$ is described. This reaction provides a convenient method for the synthesis of various per(poly)fluorocarboxylic acids under mild conditions.

INTRODUCTION

Perfluorocarboxylic acids are versatile chemicals. They are generally prepared by the electrochemical fluorination of the corresponding acyl halides. Treatment of R_fX (X=I, Br, CCl_3) with chlorosulfonic acid(1) or with oleum using Hg as a catalyst(2) is the non-electrochemical method widely used. In recent years alternative methods like treatment of R_fI with Rogalite(3), photooxidation of perhalofluorosulfinates(4) or reaction of perfluoroalkane sulfinates with various single electron oxidizing agents have appeared. In this paper, the conversion of various per(poly)fluoroalkyl halides into the corresponding carboxylic acids with different redox systems is reported.

RESULTS AND DISCUSSION

1,1,1-Trichlorotrifluoroethane (CF_3CCl_3) was taken as a model substrate in this study. When this substrate was treated with various redox systems, trifluoroacetic acid was formed. The results are listed in **Table 1**.

TABLE 1

Conversion of CF_3CCl_3 into CF_3COOH with various redox systems[a]

Entry	Oxidizing agent	Reducing agent	Time (h)	Temp. (°C)	Solvent	Conversion (%)[b]	Yield (%)[b]
1	$(NH_4)_2S_2O_8$	HCO_2Na	10	25	DMF[c]	100	95[d]
2	$(NH_4)_2S_2O_8$	oxalate	14	25	DMF	52	100
3	H_2O_2	$FeSO_4$	0.5	40	$DMF+H_2O$[e]	100	100
4	$(NH_4)_2S_2O_8$	$Na_2S_2O_4$	5	35	$DMF+H_2O$[e]	100	100
5	H_2O_2	$Na_2S_2O_4$	1	40	$DMF+H_2O$[e]	100	100
6	$KBrO_3$	$Na_2S_2O_4$	3	45	$DMF+H_2O$[e]	85	100
7	$(PhCO)_2O_2$	$PhNMe_2$	16	30	DMF	25	100

[a] CF_3CCl_3 : Oxidizing agent : Reducing agent= 1:1:1(molar ratio).
[b] Unless otherwise noted, all the conversions and the yields in this and following tables were determined by ^{19}F NMR.
[c] N,N-dimethylformamide. [d] The by-product was CF_3CCl_2H.
[e] 1:1(volume).

As shown in **Table 1**, except for entries 2 and 7, the conversion of CF_3CCl_3 into CF_3COOH with various redox systems was rather effective.

Solvent played an important role in such conversions. As shown in **Table 2**, of the following four solvents tested, DMF was found to be the best.

The conversions of various per(poly)fluoroalkyl halides into the corresponding acids with $(NH_4)_2S_2O_8/HCO_2Na.2H_2O$ are shown in **Table 3**.

TABLE 2

Effect of solvent on the conversion of CF_3CCl_3 into CF_3COOH with $(NH_4)_2S_2O_8/HCO_2Na \cdot 2H_2O$

Entry	Solvent	Temperature (°C)	Time (h)	Conversion (%)
1	DMF	25	10	100
2	CH_3CH_2OH	25	10	25
3	CH_3CN-H_2O[a]	25	15	0
4	H_2O[b]	25	10	0

[a] 1:1 by volume.

[b] Phase transfer catalyst $C_6H_5CH_2N(n-Bu)_3Cl$ was added.

TABLE 3

Conversion of per(poly)fluoroalkyl halides into the corresponding acids with $(NH_4)_2S_2O_8/HCO_2Na \cdot 2H_2O$ in DMF[a]

Entry	substrate	acid	temp. (°C)	time (h)	conversion(%)	yield (%)[b]
1	$C_6F_{13}I$	$C_5F_{11}COOH$	55	12	75	83.9
2	$Cl(CF_2)_4I$	$Cl(CF_2)_3COOH$	50	14	69	78.7
3	$Cl(CF_2)_6I$	$Cl(CF_2)_5COOH$	50	14	70	81.2
4	$I(CF_2)_6I$	$(CF_2)_4(COOH)_2$	50	12	50	92.0
5	$I(CF_2)_8I$	$(CF_2)_6(COOH)_2$	50	12	62	89.0
6	CF_3CCl_3	CF_3COOH	25	10	100	72.5
7	CF_3CBr_2Cl	CF_3COOH	50	4	100	71.8
8	$CCl_3CF_2CFClBr$	$CF_2(COOH)_2$	30	5	100	74.6
9	$CF_2(CCl_3)_2$	$CF_2(COOH)_2$	30	5	100	69.8
10	$CF_2(CFCl_2)_2$	$CF_2(COOH)_2$	50	5	100	57.3
11	$CF_2ClCFCl_2$	$ClCF_2COOH$	20	10	100	55.6
12	$CF_2BrCFClBr$	$BrCF_2COOH$	15	20	100	63.4
13	CF_2ClCCl_3	$ClCF_2COOH$	30	4	100	66.5
14	$CF_2ClCFClCF_2CFCl_2$	$CF_2ClCFClCF_2COOH$	30	5	100	78.6
15	$CF_2\!-\!CFCF_2CFCl_2$ ($\backslash O /$)	$CFCl_2CF_2COOH$	40	5	100	64.2

[a] In entries 1,2,3,6,7,11,12,13,14,15, substrate: $(NH_4)_2S_2O_8$: $HCO_2Na.2H_2O=1:1:1$ (molar ratio); In entries 4,5,8,9,10, substrate: $(NH_4)_2S_2O_8$: $HCO_2Na.2H_2O=1:2:2$(molar ratio).

[b] Isolated yield.

As shown in **Table 3**, $(NH_4)_2S_2O_8/HCO_2Na.2H_2O$ could hydrolyze not only R_fI, R_fCCl_3, $R_fCFBrCl$, and R_fCBr_2Cl into R_fCOOH, but also R_fCFCl_2 into R_fCOOH under mild conditions. Such a redox system also showed a rather good selectivity. For example, the hydrolysis of $BrCF_2CFClBr$ or $CF_2ClCFCl_2$ could be controlled, and only $BrCF_2COOH$ or $ClCF_2COOH$ was respectively obtained. However, epoxide or double bond was totally destroyed under such conditions. System like $(NH_4)_2S_2O_8/Na_2S_2O_4$ was effective for the conversion of CF_3CCl_3 into CF_3COOH (entry 4 in **Table 1**), but R_fCF_2I was deiodo-sulfinated completely in such a redox system.

Ammonium persulfate is an one-electron transfer oxidizing agent, which spontaneously produces $SO_4^{\overline{.}}$. By mixing $(NH_4)_2S_2O_8$ and HCO_2Na together, $CO_2^{\overline{.}}$ is formed**(5)**. Experiments showed that conversion of polyfluoroalkyl halides into the corresponding acids was completed only in the presence of $(NH_4)_2S_2O_8$ and HCO_2Na. This implied that such conversion was initiated by $CO_2^{\overline{.}}$ other than $SO_4^{\overline{.}}$. In addition, carbon dioxide was detected in the course of such reaction. To gather the known facts, a tentative mechanism of such reaction was depicted as follows **(scheme 1)**.

$$S_2O_8^{\overline{\overline{.}}} \longrightarrow SO_4^{\overline{.}}$$
$$SO_4^{\overline{.}} + HCO_2^- \longrightarrow HSO_4^- + CO_2^{\overline{.}}$$
$$R_fCCl_3 + CO_2^{\overline{\overline{.}}} \longrightarrow R_fCCl_2^{.} + CO_2 + Cl^-$$

$$R_fCCl_2H \qquad R_fCCl_2OOH \xrightarrow{-HOCl} R_fCOCl \xrightarrow{H_2O} R_fCOOH$$

with $\nearrow H^-$ and $\searrow O_2$ branches.
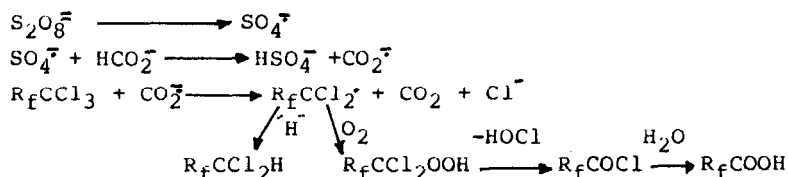
Scheme 1.

As shown in **Table 3**, the conversion of R_fI was lower than that of R_fCCl_3 even at a higher temperature and a longer reaction time. Since iodide ion is an one-electron reductant and may exhaust some $SO_4^{\overline{.}}$ **(Scheme 2)**. Thus iodide ion formed during the reaction might retard the reaction.

$$I^- + SO_4^{\overline{.}} \longrightarrow I^{.} + SO_4^{\overline{\overline{.}}}$$

$$2\,I^{.} \longrightarrow I_2$$
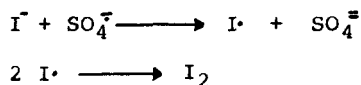
Scheme 2.

All boiling points, melting points, ^{1}H and ^{19}F NMR spectra of the known per(poly)fluorocarboxylic acids obtained are described in **Table 4**.

TABLE 4

Boiling points, melting points and ^{1}H and ^{19}F NMR spectra of per(poly)fluorocarboxylic acid

Compounds	Boiling points ($^\circ$C/mmHg)			^{19}F (ppm) (in $CDCl_3$)	^{1}H (ppm) (in $CDCl_3$)
	Found	Reported	Ref		
$C_5F_{11}COOH$	74–76/60	157	6	5.3(3F)	
				43(2F)	10.69
				46.5(4F)	
				51.5(2F)	
$Cl(CF_2)_3COOH$	93–95/5	83/3	7	–9.5(2F)	
				40.2(2F)	10.96
				43.1(2F)	
$Cl(CF_2)_5COOH$	107–110/5	79/1	7	–9.3(2F)	
				40.4(2F)	11.39
				43.0(2F)	
				44.9(2F)	
				52.2(2F)	
CF_3COOH	69–71	72.4	8	0	10.84
$ClCF_2COOH$	119–120	121.5	9	–11.6	10.28
$BrCF_2COOH$	73–75/100	145–147	10	–14.01	10.04
$CFCl_2CF_2COOH$	68–71/10	83–85/20	11	–3.7(1F)	12.18
				36.3(2F)	
$CF_2ClCFClCF_2COOH$	78–80/10	98–100/23	11	–13(2F)	10.65
				38.1,40.7	
				(2F,AB.J=263.2Hz)	
				54(1F)	
$CF_2(COOH)_2$	115–118[a]	117–118[a]	6	44	11.70
$(CF_2)_4(COOH)_2$	130–131[a]	132–134[a]	6	40.7(4F)	10.4
				46.3(4F)	
$(CF_2)_6(COOH)_2$	150–152[a]	154–158[a]	6	43.5(4F)	11.7
				47.8(8F)	

[a] Melting point.

EXPERIMENTAL

Boiling points and melting points were uncorrected. ^{1}H NMR(with chemical shifts in ppm from external TMS) and ^{19}F NMR(with chemical shifts in ppm from external TFA and positive for upfield shifts) were recorded on a Varian EM-360 spectrometer. (60Mz for ^{1}H and 56.4Mz for ^{19}F).

All materials were commercial grade and were used without further purification. All organofluorine compounds were prepared by known methods. The experimental conditions used for these hydrolyses are compiled in **Table 3**.

Typical procedure: 4g(21.3mmol)CF_3CCl_3, 5g(21.9mmol)$(NH_4)_2S_2O_8$, 2.3g(22.1mmol) $HCO_2Na.2H_2O$, and 40ml DMF were stirred at 25°C for 10 h with air bubbling. After that the reaction mixture was poured into water and the strongly acidic solution was extracted with ether. The ether extract was neutralized with aqueous $NaHCO_3$. The separated water layer was evaporated to dryness. The residue was mainly CF_3COONa. Distillation of the formed CF_3COONa with 5ml concentrated sulphuric acid gave 1.8g CF_3COOH(72.5% yield).

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